SELECTIVE OXIDATION OF BUTENES TO MALEIC ANHYDRIDE OVER VANADYL PHOSPHATE CATALYST

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CERTIFICATE

It is certified that the work 'SELECTIVE OXIDATION OF BUTENES TO MALEIC ANHYDRIDE OVER VANADYL PHOSPHATE CATALYST' has been carried out under my supervision and has not been submitted elsewhere for a degree.

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ACKNOWLEDGEMENTS

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NOMENCLATURE

A_i	ith component in the reaction network
A_j^o	pre-exponential factor in the Arrhenius rate expression
E_j	Energy of activation for the reaction step j, cal./g.mole
F_t	Total molar flow rate, g.moles/sec
Fo_1	Total molar flow rate for component A_1 in feed, gmoles/sec.
K_j	reaction rate constant for the step j, g.moles/g.cat. atm.sec.
No_1	Mole fraction of the component A_1 in feed, Fo_1/F_t
n	Reaction order
P	Total pressure, atm
p_i	Partial pressure of the component A_i, atm
po_1	Partial pressure of the component A_1 in feed, atm
R_i	reaction rate of species A_i, g.moles/g.cat.sec.
R_g	Gas constant, cal./gmole
W	Weight of the catalyst gm.
X	Conversion of the component A_1
Y_i	Yield of component i

Subscripts

b	bulk fluid conditions
i	designating which component
j	designating which reaction

ABSTRACT

Selective oxidation of butenes to maleic anhydride over vanadyl phosphate catalyst has been investigated in an isothermal packed bed reactor. Effect of reducing agent for ammonium meta vanadate in the preparation of the catalyst has been studied and d-tartaric acid has been found to be the best among the three different acids used. Addition of lithium hydroxide to vanadyl phosphate has been found to increase the yield of maleic anhydride from 42.5 per cent to 48.5 per cent at $360^{\circ}C$. Kinetics of the butene oxidation has been investigated using VPLiOH catalyst (P:V:Li = 1.6:1.0: 0.5) in the temperature range $350-390^{\circ}C$ at 0.9 per cent mole butene in air. Rate constants and energies of activation have been obtained by using the following reaction scheme:

Butene $\xrightarrow{k_1}$ Butadiene $\xrightarrow{k_3}$ Maleic Anhydride

I, II k_2, IV k_4, III, V k_5 → Oxides of carbon
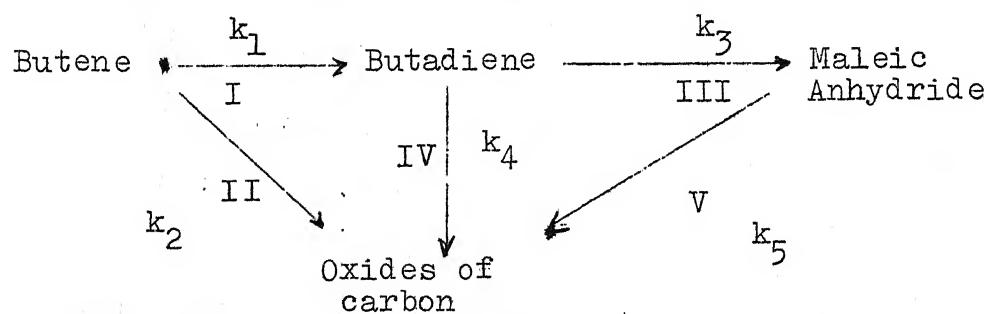
The rate constants computed at 350, 370, $390^{\circ}C$ followed the Arrhenius behaviour. Estimated values of the energies of activation were found to be E(I)=11.9, E(II)=7.41, E(III)=22.9 E(IV)=5.75, E(V) = 13.62 Kcal/g.mole. The reaction step III was found to be highly temperature sensitive relative to other steps.

CHAPTER 1

INTRODUCTION

1.1 Introduction:

Maleic anhydride is an important chemical for the production of alkyd resins, polyester resins, lacquors, fumaric acid, food additives, agricultural chemicals [1,2] etc. Vapour phase oxidation of butenes obtained from C_4 hydrocarbon fraction is a commercially desirable process for the manufacture of maleic anhydride. Although the yield of maleic anhydride is lower as compared to the benzene process [3], the process looks attractive due to the fact that the benzene being a precurser for many other important chemicals its availability is limited. Besides this, C_4 fraction is cheaper than the benzene [4] and all the four carbon atoms are utilized in its oxidation to maleic anhydride.

Although commercially successful implementation of this process has been done by Mitsubishi Chemical Industry [5] and Bayer A.G. [6], many other organizations like, BASF, Cheveron, Monsanto, Ube, Kuraray are actively engaged in the process development work. Bulk of the available literature deals with the development of active and selective oxidation catalyst for converting C_4 fraction to maleic anhydride

1.2 Literature Review:

With the motive of making C_4 process give yields comparative to benzene process, it has long been a process research goal to search for a catalyst which gives increased yields of the maleic anhydride, and has a longer life. Extensive review dealing with the recent developments in the C_4 process has been done by Varma and Saraf [6]. A few of the industrial catalyst compositions are given in the Table 1.1.

The $V_2O_5-P_2O_5$ system is often used for the oxidation of butenes. Extensive review of numerous $V_2O_5-P_2O_5$ patented catalysts has appeared in the previous reviews [7,8]. Other catalysts have also been used for the butene oxidation but to a lesser extent.

$V_2O_5-MoO_3$ system of catalysts has been studied extensively by Blanchard and Delgrange [9] and also by Jascai [10] and it has been reported that maximum activity and selectivity towards maleic anhydride is obtained by catalyst containing 25 per cent. MoO_3[11]. Other systems like $Bi_2O_3-MoO_3-P_2O_5$, Co-Mo oxides have also been used for the oxidation of butenes to maleic anhydride [12, 13].

$P_2O_5-V_2O_5$ system has been studied by Ai [14] and Ostraushko [15]. These workers have reported that the activity of such catalysts decreases as compared to the V_2O_5 catalyst but the selectivity towards formation of maleic anhydride increases. The preferred atomic ratio of P:V in the vanadyl

TABLE 1.1: SOME OF THE COMMERCIAL CATALYST CONFIGURATIONS FOR OXIDATION OF BUTENES TO MALEIC ANHYDRIDE

Organization	Catalyst composition	$T^{o}C$	Contact time, secs.	Feed gas composition	Butene conversion, per cent	Yield of maleic anhydride, per cent	Reference
1	2	3	4	5	6	7	8
Princeton Chem. Res. Inc.	P-V-O P:V=1.75	400		Butene-Air			U.S.Patent 3,293,268(1966) Pergmann R.I. and Frish N.W.
ICI Ltd.	Mo-TeO$_2$	425	1.5	2 per cent v.butenes 92 per cent v-2-CuH$_8$ 50 per cent v H$_2$O, 10 per cent, v O$_2$,28 per cent,v H$_2$		30	Neth. Appl. 6,514,701(1966) ICI Ltd.
ICI Ltd.	18 per cent V$_2$O$_5$-P$_2$O$_5$ 4:5 molar ratio supported on Al$_2$O$_3$ having a range of surface area S$_A$=75 m²-gm-1	272/322	2.5	0.7per cent butene in air	88	12.8	
	20 m² gm-1	248/275	2.5	0.7 per cent v on butene in air	70	21.6	

Table 1.1: (contd)

1	2	3	4	5	6	7	8
	1.5 m² gm⁻¹	385/423	2.5	1.0 per cent v butene in air	100	25.9	
	0.4 m² gm⁻¹	500/524	0.8	0.6 per cent v butene in air	100	36.4	
	0.1 m² gm⁻¹	450/500	1.2	0.7 per cent v butene in air	100	46.7	
ICI Ltd.	Cobalt Molybdate/glass helics	400	6	1.5 per cent v C-2-C_4H_8 35 per cent H_2O, air	63.5	47	Brit.Patent 1,155,176 (1969) Ger.Offen 1,951,537 (1970)
Mitsubishi Chem.Ind.Co. Ltd.	V_2O_5:P_2O_5 P:V=2/silica	405-420		4 per cent m 'butene' mixture in air containing 18.4 per cent m, 1-C_4H_8 13.0 per cent m, C_4H_8 8 per cent m, C_4H_6 7.0 per cent m C_4H_{10} 29.0 per cent m iso C_4H_8		46	
Petro Tex Chem.Corporn.V:P:Nb+ 1.0:1.3:0.0375 on alundum	20 per cent	406		0.7percent m to 0.75 per cent m 2-C_4H_8 in air		88	US Patent 3,255,211(1966)
	V:P:Cu:Nb 1.0:1.35:0.032:0.02	446	0.7	0.7 per cent 2-C_4H_8 in air		84	US Patent 3,255,212 Kerr R.O. (1966)

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Table 1.1 (contd)

1	2	3	4	5	6	7	8
	P:V:Cu:Nb:Li 1.45:1.0:0.036: 0.022:0.068	446		0.7percent m 2-C_4H_8 in air		87	US Patent Kerr R.O. (1966)
	P:V:Cu:Li 1.0:1.4:0.024: 0.072	446		-do-		-92	US Patent Kerr R.O.
	P:V:O + 0.003-0.125 atom K/atom of P	480		-do-		-87	US Patent 3,288,721
	20 per cent V_2O_5:PO(1:1.2) +1per cent w Li/Alundum	550		0.7 per cent m 2 C_4H_8 in air 92 gm 2-C_4H_8/l cat/h		-93	Brit Patent 1,095,233 1967 Petro Tex Chem. Corpn.
BASF A.G.	4 per cent V_2O_5,10 per cent w, P_2O_5, 86 per cent w TeO_2	452	8.62g/hr 1 l/hr butene mix. 57 per cent v 1-C_4H_8 7.6 per cent v C-2-C_4H_8 12.8 per cent v t-2-C_4H_8		7	7.7 kg/hr	Belg.Pat. 666,519, (1968) Ger.Pat. 1,443,452 (1970) -Nonemacher H. Appl.M. witness of Hang J.
	2-5per cent V_2O_5, 5-10 per cent P_2O_5 80-86 per cent w Andtase	340	-do-			56.5	Ger.Offen 2,030,201 (1971) Engelbach H.,Stoess& H. and RenaurE.

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Table 1.1 (contd)

1	2	3	4	5	6	7	8
BASF Alr.	V_2O_5(8.1 per cent), WO_3(2.5 per cent), P_2O_5(11.9 per cent), NiO(4.5 per cent), TiO_2(73 per cent)	450	$29.3 \ g/m^{-1}$ Butenes and air 1200 l/hr			25.5 g/hr	Brit.Pat. 1,154,148 (1969) and Fr.Pat. 1,495,765 (1967)

phosphate catalyst is 1.1 to 1.6. At P:V=1.6, further destruction of maleic anhydride is insignificant [16]. The beneficial action of phosphorous addition to the V_2O_5 catalyst is its control over the side reactions occurring parallel to the maleic anhydride formation. Kerr [17] has reported that maximum yield of maleic anhydride is obtained when vanadium has an average valency less than plus five. This valency can be controlled [18] by method of preparation of the catalyst or by changing the hydrocarbon concentration in the feed [19].

Method of preparation of the catalyst plays an important role in determination of the activity and selectivity of the catalyst. Commonly used method involves dissolving a vanadium containing compound such as ammonium-meta vanadate in a reducing agent then adding a phosphorous compound such as phosphoric acid or P_2O_5 and then depositing the complex formed on the carrier and drying. The second procedure involves mixing of ammonium meta vanadate and phosphoric acid in the presence of a carrier followed by precipitation of actives on the carrier. The catalysts prepared by former method have been reported [20] to give higher yields of maleic anhydride.

Inorganic acids such as hydrochloric acid, and organic acids such as oxalic acid are used for reducing ammonium meta vanadate. Recently d-tartaric acid has been used [21]

as the reducing agent. Improved activity and selectivity
have been reported by Nakamura [22] for this catalyst.
Structural difference between the catalysts prepared from
d-tartaric acid; citric acid, maleic acid and oxalic acid
has been pointed out by the same author.

It has been reported by Kerr [23] that the $V_2O_5-P_2O_5$
catalysts loose their activity after about 300 hours. of
operation and is attributed to the loss of phosphorous.
Alkali metal compounds such as potassium chloride, lithium
hydroxide [24] are added to stabilize phosphorous.

Addition of lithium hydroxide considerably increases
the catalyst life. A lithium stabilized catalyst shows
less than 10 per cent decrease in the yield of maleic anhydride
after about 1700 hrs of operation [25]. It has also been
reported that addition of small amount of copper along with
lithium increased the catalyst life to 3500 hrs. and the yield
of maleic anhydride showed no sign of detoriation. Study of
alkali metal addition in the light of activity and selectivity
has been done by Ai [26] who reported that the addition of
less than 10 per cent lithium hydroxide had no effect on the
yield of maleic anhydride but addition of sodium or potassium
(Na:V or K:V = 0.2) considerably lowered the oxidation activity.
Similar results for the catalyst oxidizing benzene to maleic
anhydride has been reported by Egbert [27].

Ikawa and Yamamoto [28] have however contradicted the above results of Ai. These workers have found a V_2O_5: P_2O_5 catalyst (atomic ratios P:V:Li=1.5:1.0:0.5) to give increased yields (62.3 per cent mole) as compared to yield (49.3 per cent) obtained under similar conditions without LiOH.

1.3. Objective of the Work:

The present investigation is aimed to achieve two objectives. The first being to see the effect of reducing agents and the addition of lithium hydroxide on the yield of maleic anhydride over vanadyl phosphate catalyst.

The second one is to study the basic kinetic parameters of butene oxidation to maleic anhydride over a selected catalyst in an isothermal integral reactor.

CHAPTER 2

EXPERIMENTAL

2.1 Catalyst Preparation:

Following four compositions were prepared in the laboratory:

1. OA[b] -VP-LiOH   P:V:Li = 1.6:1.0:0.5
2. TA[a] -VP-LiOH   P:V:Li = 1.6:1:0.5
3. TA-VP   P:V = 1.6
4. HCl-VP   P:V = 1.6

[a] d-Tartaric acid as reducing agent

[b] oxalic acid as reducing agent

[c] hydrochloric acid

Since the procedure for the preparation of these catalysts is the same it will be described for the catalyst no.1. only 57.5 gram of ammonium meta vanadate with 120 gms of oxalic acid were dissolved with distilled water and the mixture was refluxed till 600ml. of clear blue solution was obtained. The blue colour indicated that the valency of the vanadium was less than plus five. To this solution 3.7 gms of $LiOH \cdot H_2O$ and 55.9 gms of P_2O_5 were added cautiously and the mixture was again refluxed for about 12 hours so as to form the vanadyl phosphate complex which was then deposited on the 250 gms of the silica gel carrier of -8 + 10 mesh size. The mixture was then dried in a rotary vacuum dryer. This ensured uniform deposition of the complex on the support

the free flowing catalyst was then dried at $130^{\circ}C$ and then calcined at $500^{\circ}C$ for 5 hours. The catalyst so prepared was then crushed, sieved, and stored in the well stoppered bottles for subsequent usage.

In the preparation of the second catalyst d-tartaric acid was the reducing agent for ammonium meta vanadate instead of oxalic acid. Rest of the procedure was same as that given above. In the third and fourth catalysts no LiOH was added. The last one was prepared using hydrochloric acid as the reducing agent.

2.2 Catalyst Characterization

X-Ray Analysis: X-ray diffraction patterns of all the catalyst samples in the 2θ range of 6° to 60° were recorded using GEC XRD-VI generator, SPG-4 detector and SPG-2 diffractometer using copper (K_α) radiation. The diffractometer was operated at 2° diverging and receiving slits at scan rate of 1° per minute and a continuous trace of intensity as a function of 2θ was recorded.

IR Spectra: IR spectra of the powdered catalyst samples were recorded on a Perkin Elmer grating spectrophotometer using KBr disc technique.

Surface Area and Pore Volume: Surface area of the powdered samples were calculated from the nitrogen adsorption isotherm using BET technique. Mercury porosimeter Carlo-Erba model 70, in the range 2000 atmospheres was used for measuring pore volume and pore size distribution.

2.3 Butene Oxidation:

2.3.1 Feed Specifications

Compressed air was used as a source of oxygen carbon-dioxide and moisture were removed before passing it through the system. Secondary butanol was dehydrated by using 60 per cent sulfuric acid at a temperature below $160^\circ C$ for generation of butenes. It has been reported that the butenes generated by this method are essentially free from 1-butene (28). A typical composition revealed 53.8 per cent t-2-butene, 41.1 per cent cis-2-butene, and 5.1 per cent 1-butene.

2.3.2 Experimental Set-Up:

The apparatus used for the oxidation of butene is depicted in the Figure 2.1 as a flow diagram. It consisted of the two independent flow systems for butene and air, leading to a mixing chamber J. Butene from the dehydration apparatus was stored in the butene storage drum B by downword displacement of water. The butene was displaced from the drum by using water from constant level overhead tank when required. The flow rate of butene was controlled through the needle valves V_2 and V_3 before passing it to the mixing chamber J. The flow rate of butene was measured accurately using a calibrated rotameter R1. The gas was dried by passing it through the bed anhydrite D_2 (A drying agent with colour indication) before passing it through the system. The compressed air was passed through the potassium hydroxide

scrubber K to remove carbon-di-oxide and then to dryer D1
to remove any moisture. The flow rate of air to the system
was controlled through the needle valves V_1 and V_3. A
capillary C1 was introduced in the air path to measure the
flow rate of air prior to its introduction to the mixing
chamber. The pressure drop across the capillary was measured
by mercury manometer M_1. Air-butene mixture after mixing
chamber was passed to the preheater P through a calibrated
rotameter R2 and a needle valve V_5. A mercury manometer M2
was provided to measure the pressure at the inlet. Gas
sampling port S_1 was provided for collecting feed gas samples
for chromatographic analysis. Needle valve V_4 was used as a vent.
Flow rate of air-butene mixture to the reactor could be
manipulated through valve V_4 without changing the composition
of the gases in the mixture.

Preheater, reactor assembly was made of SS 316 type
seamless tube having ID = 6.35 mm. The preheater P was a
coil of 125 mm ID connected to the reactor through a swage
lok joint. Reactor R was a 300 mm long tube provided with a
wire mesh M for supporting the catalyst bed. Two protected
thermocouples T_1 and T_2 were provided along the length of the
reactor. T_1 was used to measure the catalyst bed temperature
where as T_2 was used to measure the reactor effluent tempera-
ture Preheater-Reactor assembly was immersed in the mixture
of the molten salts. Kept in the cylindrical vessel Q. The

composition of the salt bath was 51 per cent potassium nitrate, 42 per cent sodium nitrite, 7 per cent sodium nitrate (melting point $150^{\circ}C$). Immersion heater E of 2000 watt capacity was used for heating the salt bath and the temperature was measured at several locations. All the thermocouples were connected to the multipoint temperature indicator F. Temperature of the salt bath was controlled using a sensitive temperature controller TC within $\pm 1^{\circ}C$. The salt bath was agitated by stirrer S.

Stainless steel tube of 3/16" ID carrying reactor effluents to the product recovery train was heated by the floxotherm heating cord input to which was controlled through a variable autotransformer. Effluents through the reactor could be channeled through two alternate routes by suitably adjusting the valves V_6 and V_8. Before steady state was attained the effluents were allowed to take the presteady state train which passed through valve V_6 a cold trap I1, and gas sampling port S2 in series.

The steady state train contained four 175 ml. glass bubbler U, cold trap I2, dryer D3, gas sampling port S3 and the capillary C2 in series. Pressure drop across the capillary was measured by the manometer M3. The capillary off gases were then metered by wet test meter and then vented to the atmosphere. The exit gas composition was measured by the Orsat apparatus G.

2.3.3 Operating Procedure:

The reactor was loaded with the fresh catalyst of required size, diluted with the porcelain beads of same size. A wire mesh and more amount of porcelain beads were kept on the top of the catalyst bed inorder to keep the bed in static condition. The catalyst bed was first heated the presence of the flowing air, Once the desired temperature was obtained then butene was also admitted to the mixing chamber. The mole ratio of these gases in the mixture was altered by changing the flow rates. During the initial period the reactor effluents were diverted to the presteady state train through the valve V_6 keeping V_8 closed. Analysis of the exit gas was made periodically. The steady state was realised not only from reactor temperatures getting constant but also from the exit gas composition. Once the steady state was achieved the flow was diverted to the steady state run train through valve V_8 keeping V_6 closed. The total run time varied from 15 minutes to 30 minutes depending upon the product required for analysis.

2.3.4 Analysis:

At the end of run the scrubber solution was collected and made upto the definite volume using distilled water. Small portions of these were tested for carbonyls by oxine method. Maleic acid was estimated by titrating the scrubber solution with the standard dilute sodium hydroxide using

phenolphthalein as indicator. In a few test runs, maleic
acid was estimated as barium maleate by precipitating it as
barium maleate monohydrate (29). Since this method gave
same amount of acid as the titration, it was assumed that
there was no acetic acid formed in the measurable quantities.
Analysis of the unconverted butenes and the intermediate
product butadiene was performed on a CIC gas chromatograph.
Details of the operating conditions are given in the Table 2.1.
Carbon-di-oxide, carbon monoxide and oxygen in the effluent
streams were measured by Orsat apparatus. The absorbants
for these gases were 30 per cent potassium hydroxide, acid
cuprous chloride solution and alkaline pyrogallol respectively(30
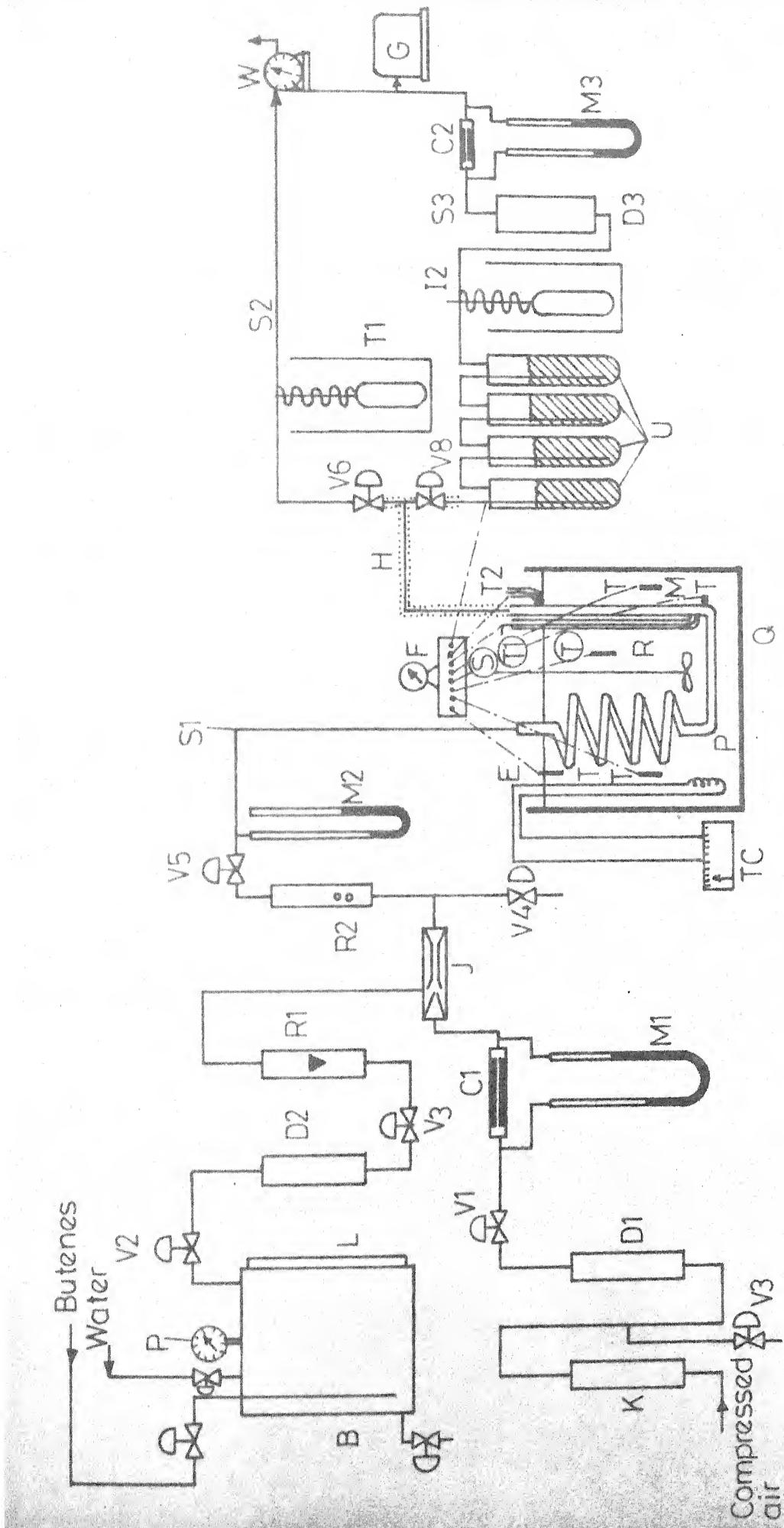
Fig. 2.1 – Flow diagram of experimental setup.

KEY TO FIGURE 2.1

B	Butene storage drum
C1 C2	Capillary tubes
D1 D2 D3	Dryers
E	Immersion heater
F	Multipoint temperature indicator
G	Orsat apparatus
H	Heating cord
I1, I2	Cold traps
J	Mixing chamber
K	CO_2 scrubber
L	Water level indicator
M1, M2, M3	Manometers
M	Mesh
P	Preheater
Q	Salt bath
R	Reactor
S1, S2, S3	Gas sampling ports
T	Thermocouples
U	Bubbler
W	Wet test meter

TABLE 2.1 : OPERATING CONDITIONS FOR THE CHROMATOGRAPH

Column	15 per cent liquid paraffin on the alumina (-100 + 120) mesh
	Length - 8 ft
	ID - 0.1875 inches
Chromatograph	CIC Baroda India Ltd.
	Detector-Thermal conductivity cell
	Recorder - E.H. Sargent
	Speed - 0.5" /min.
	Filament current - 110 mA
	Attainuetion - 1
Carrier Gas	Hydrogen
	Flow rate 45 cc/min
Sample size:	5.00 cc
Retention times:	Air 1.2 min
	1-Butene 16.0 min
	Trans-2-butene 18.0 min
	Cis-2-butene 21.0 min
	Butadiene 24.6 min

CHAPTER 3

RESULTS AND DISCUSSION

Selective oxidation of butenes to maleic anhydride was investigated in an isothermal integral reactor immersed in a molten salt bath. The oxidation products were maleic anhydride, butadiene, unconverted butenes, and oxides of carbon. Acetic acid was detected but was not formed in any measurable amount. The inertness of the system was checked by passing air/butene mixture through the system without the catalyst and no oxidation product was detected. The following range of variables were covered during experimentation.

Time factor $\qquad$ $2 \times 10^3 - 11 \times 10^3$ gm cat sec/gm.mole

Temperature $\qquad$ $330^\circ C - 360^\circ C$

Concentration of butene: 0.9 per cent m in air

Yield of component i was calculated as

$$Y_i = \frac{\text{Moles of the component } A_i \text{ formed}}{\text{Moles of reactant fed} \times \delta}$$

where A_1 = moles of butene

$$\delta = \frac{\text{No. of carbon atoms in feed}}{\text{No. of carbon atoms in product}}$$

Conversion of butene = $X = (1-Y_1)$

The rate of chemical reaction for the species A_i is given by

$$R_i = \frac{1}{F_{ol}} \cdot \frac{d(F_i/\delta)}{d(W/F_{ol})} = \frac{dY_i}{d(W/F_{ol})} = \frac{dY_i}{d\tau_1}$$

where, R_i = Rate of reaction for species A_i

F_{ol} = Number of moles of butene

F_i = Molar flow rate of component A_i

W = Weight of the catalyst

τ_1 =   based upon the butene feed rate.

3.1 Four Stages of Experiments:

1. To study the effect of reducing agents on the yield of maleic anhydride.

2. To study the effect of lithium hydroxide addition on the yield of maleic anhydride.

3. Selection of process conditions for kinetic analysis

4. Kinetic experiments.

3.1.1 Effect of reducing agents for ammonium meta vanadate on the yield of maleic anhydride:

In the present investigation d-tartaric acid, oxalic acid and hydrochloric acid were used for the reduction of ammonium meta vanadate. The yield of maleic anhydride was found to be higher on the catalyst prepared from the d-tartaric acid as the reducing agent as compared to oxalic acid and hydrochloric acid (Figures 3.1, 3.2). These results are in accordance with the findings of Nakamura [21] who have reported the structural difference between the catalysts prepared by these reducing agents.
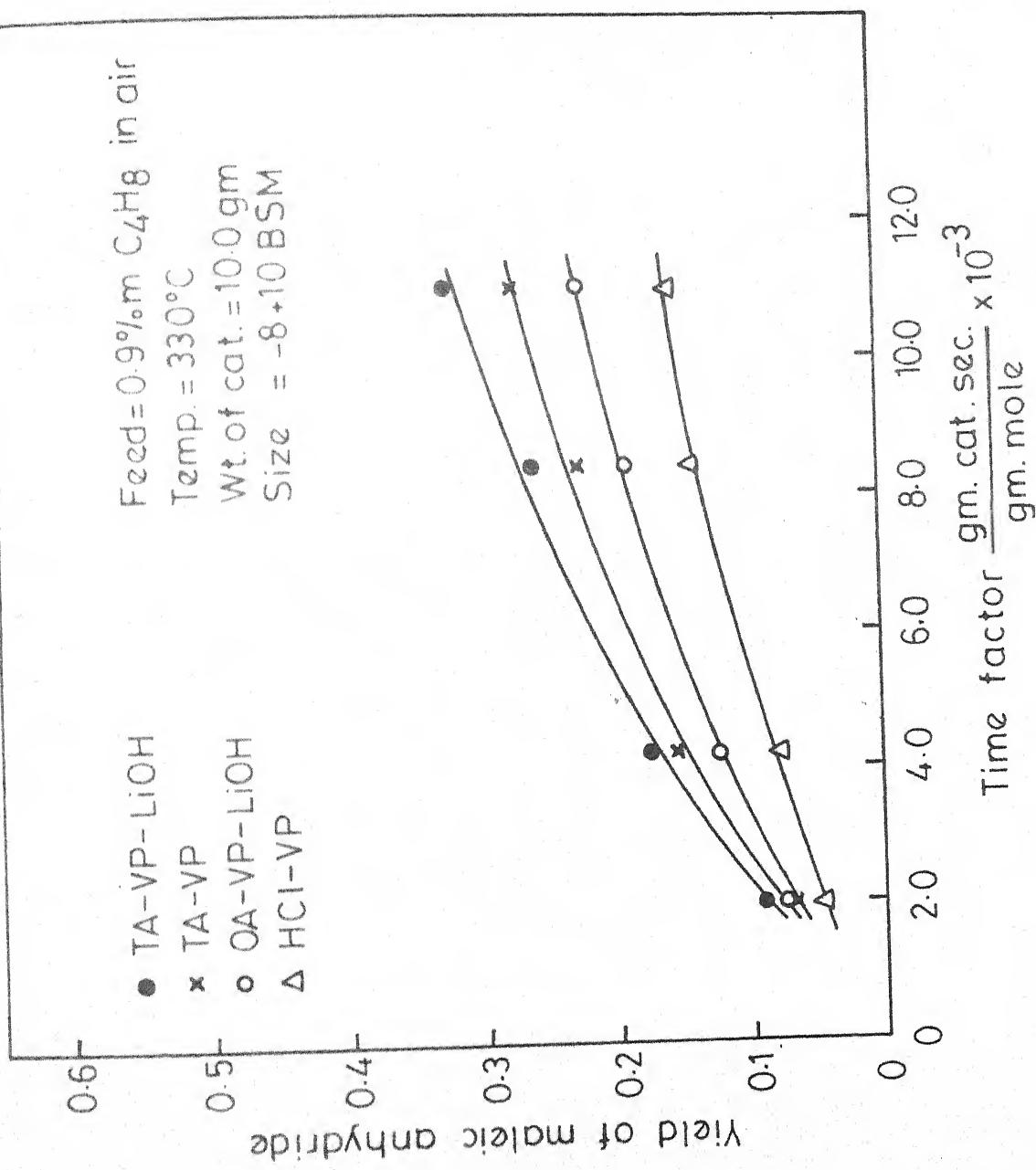
Fig. 3.1 - Yield of maleic anhydride over various catalysts vs. contact time.
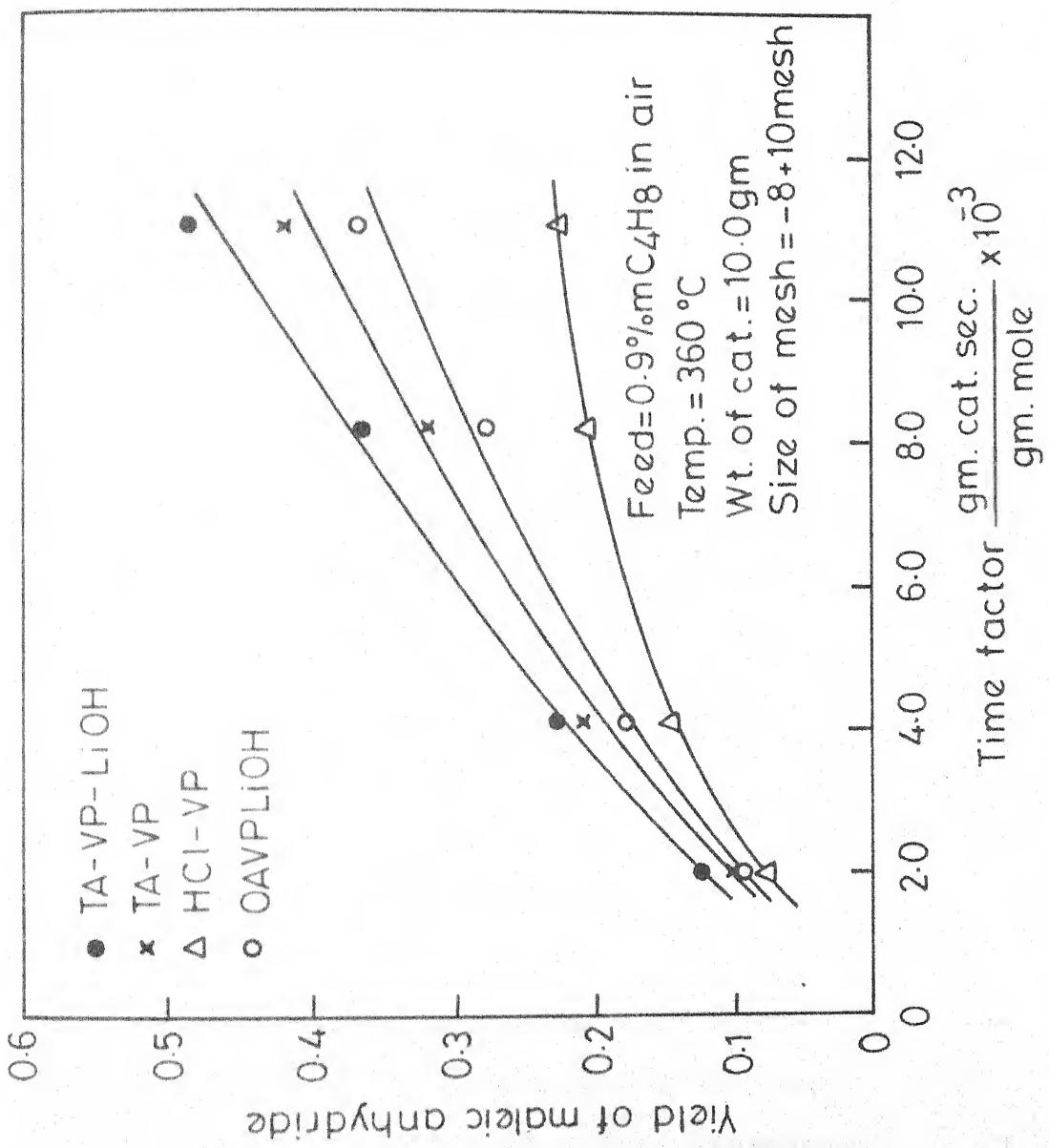
Fig. 3·2 – Yield of maleic anhydride over various catalysts vs. contact time.

X-ray and IR analysis of all the four (Figures 3.3, 3.4) catalyst samples were done. Absence of any strong diffraction pattern in x-ray analysis showed that the catalysts were essentially in the amorphous state. It has been reported that the amorphous catalysts are highly selective towards the formation of maleic anhydride [21]. IR spectra of the catalysts showed that there were absorption bands at about 820 cm^{-1}, 990 cm^{-1}, attributable to V-O-V stretching and V=O stretching vibration respectively. The broad band at about 1110 cm^{-1} is attributable to P-O stretching vibration [31]. Physical properties of catalyst are given in Table 3.1.

3.1.2 Effect of lithium hydroxide addition on the yield of

maleic anhydride:

It was observed that the yield of maleic anhydride increased with the addition of lithium hydroxide to the catalysts prepared from d-tartaric acid and oxalic acid as the reducing agents for ammonium meta vanadate (Figures 3.1, 3.2). These results are in accordance with the findings of Ikawa and Yamamoto who have reported increased yield of maleic anhydride. Ai[24] has reported that there is no significant effect of lithium hydroxide addition on the yield of maleic anhydride. Present study however indicate that definite enhahancement in the yield of maleic anhydride can be obtained by LiOH addition.
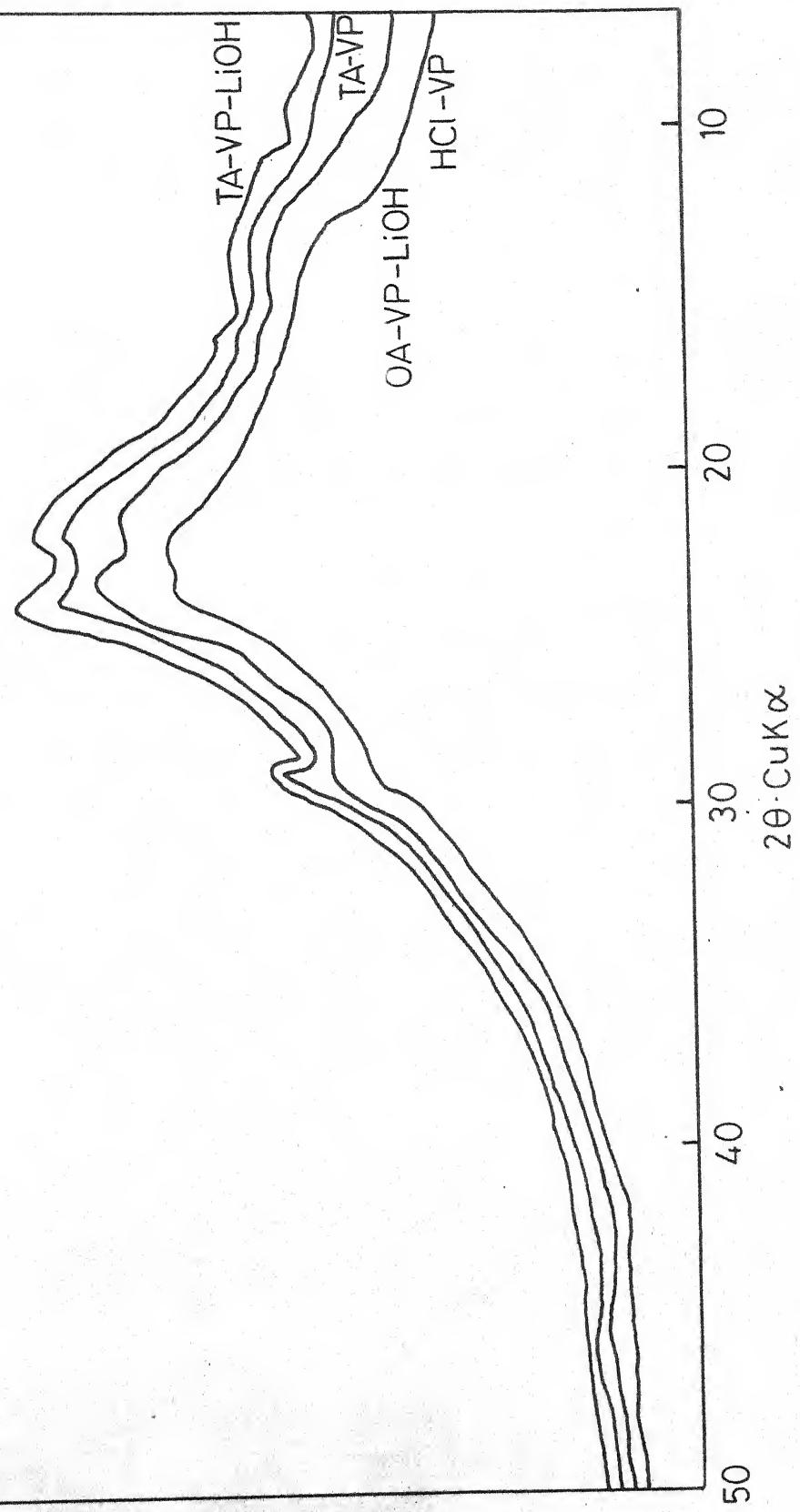
Fig. 3.3 – X-ray diffraction pattern of vanadyl phosphate catalyst.
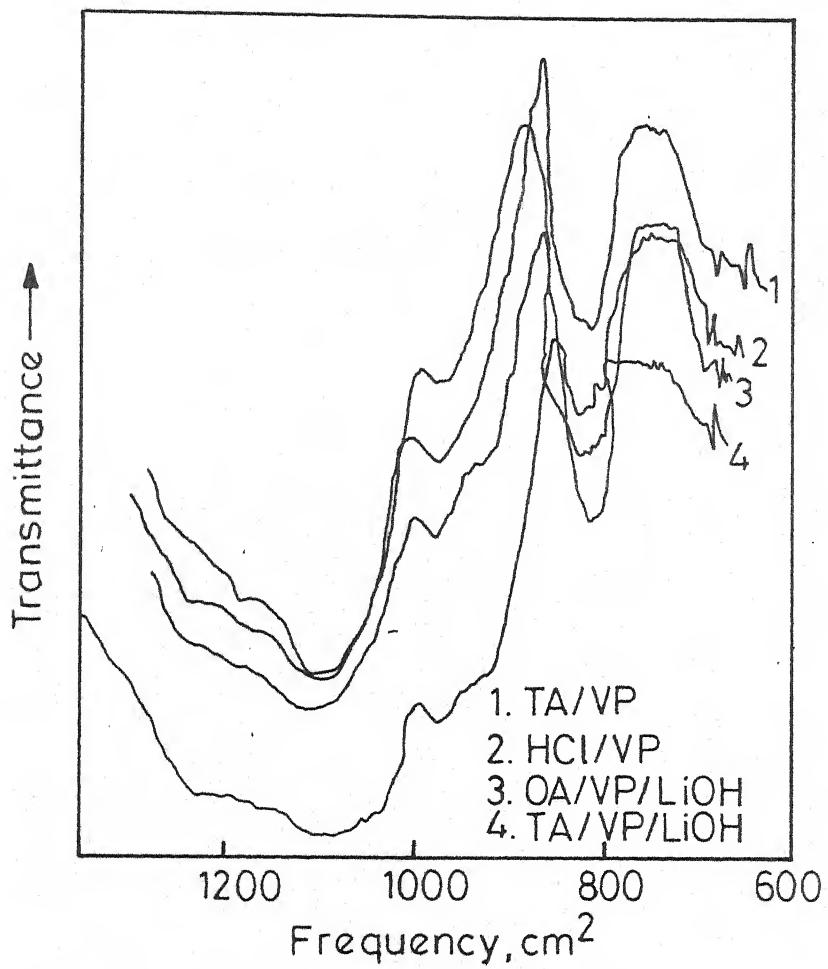
Fig. 3·4 – I.R. spectra of all 4 catalyst samples.

TABLE 3.1

PHYSICAL PROPERTIES OF THE CATALYSTS

Surface Areas	m^2/gm
TA-VPLiOH	139.9
OA-VPLiOH	104.2
TA-VP	124.7
HCl-VP	131.3

For TA-VPLiOH   Total pore volume   = 6.4779 cc/gm

                     Apparent density   = 1.09 gm/cc

                     True density   = 2.26 gm/cc

Pore Size Distribution, per cent by Volume

4-60 Å	60-100 Å	100-200 Å	200-300Å	300-400Å	400-500Å	500-75000Å
87.0	4.5	1.8	0.4	0.0	1.1	5.2

3.1.3 Selection of process conditions:

Experiments were conducted to choose a catalyst which gives high selectivity under total butene conversion and also to see if the transport effects are significant, VP-LiOH catalyst using d-tartaric acid as reducing agent was found to be the best among the catalysts studied and hence was chosen for the detailed kinetic analysis. Transport effects are tobe eliminated otherwise they would obscure the kinetics of the reaction.

Reactions were carried over TA-VPLiOH catalyst with two different lengths of catalyst beds and two different particle sizes. The fact that in the time factor range of 1×10^3 to 2×10^3 gm cat sec/gm mole (Figure 3.5) all the points were represented by a single straight line indicated that these effects were minimum in this region and hence was chosen for kinetic investigation.

3.1.4 Kinetic Experiments:

Kinetic experiments were conducted over TA-VPLiOH catalyst in the temperature range 350-390°C using 0.9 per cent mole butene in air since this concentration has been reported to be optimum by previous investigator [32]. The time factors used in these experiments were in the range 1×10^3 - 2×10^3 gm cat sec/gm mole as discussed above. 1.5 gm of catalyst was used with particles in the size range -32 + 44.
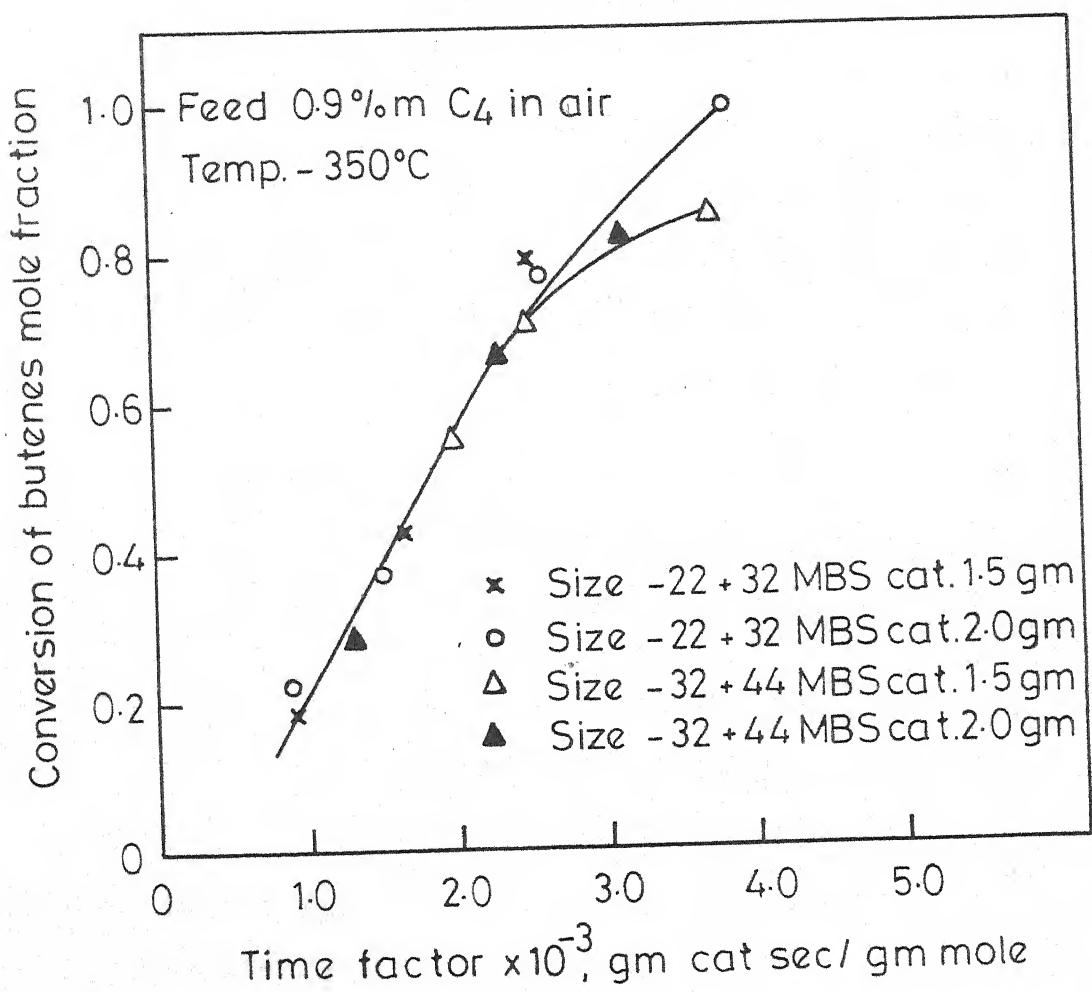
Fig. 3.5 – Testing for transport effects in butene oxidation.

3.2 <u>Kinetic Analysis</u>:

As mentioned earlier, a packed bed of catalyst was employed in the present study. A major problem in the use of packed bed is the isothermality and it was obtained by removing heat efficiently at the walls by molten salt bath which was efficiently agitated and maintained within $\pm 1^oC$. The catalyst bed was diluted by porcelain beads of same size as the catalyst particles to avoid the hot spots. Nitrogen in the feed also helped in achieving the isothermality. In the previous investigation [32] reactor of 1 inch diameter was employed and since this reaction is highly exothermic there may be radial temperature gradients. In the present study a reactor tube of smaller diameter (0.25 inch) was used. Channelling effects along the walls of the tube were also minimized by keeping the tube to particle diameter ratio atleast ten-Axial temperature gradients were minimized by employing a small length of catalyst bed.

3.2.1 Product distribution:

A typical product distribution at 350^oC is given in Figure 3.6. Similar trend is observed at 370^oC and 390^oC while the yields of maleic anhydride and carbon oxides steadily increased with increase in the time factor, butadiene showed a maximum, typical of an intermediate. Figures 3.7 to 3.9 show yields of individual products at different temperatures.
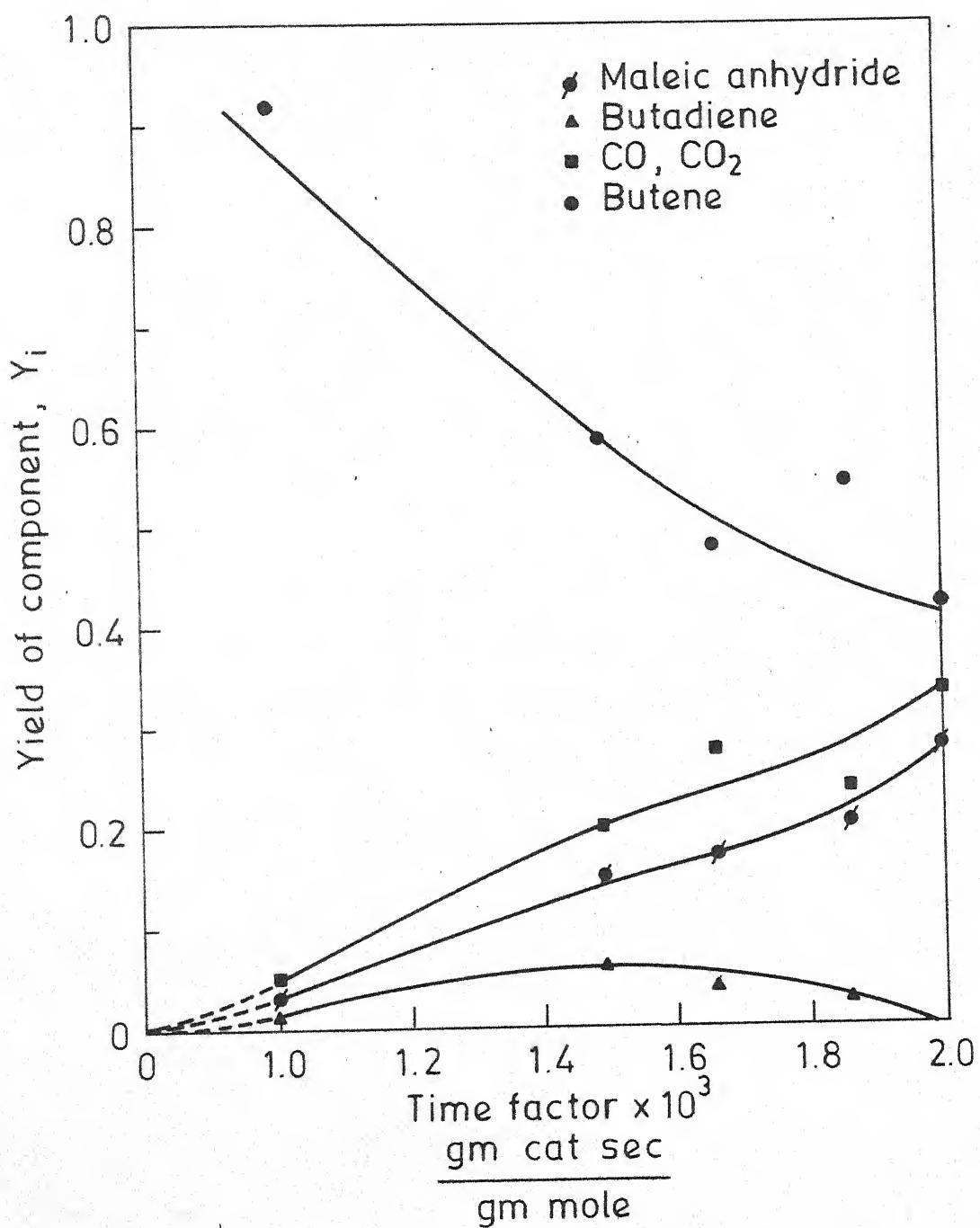
Fig. 3.6 A typical product distribution at 350 °C over TA - VP - LiOH catalyst.
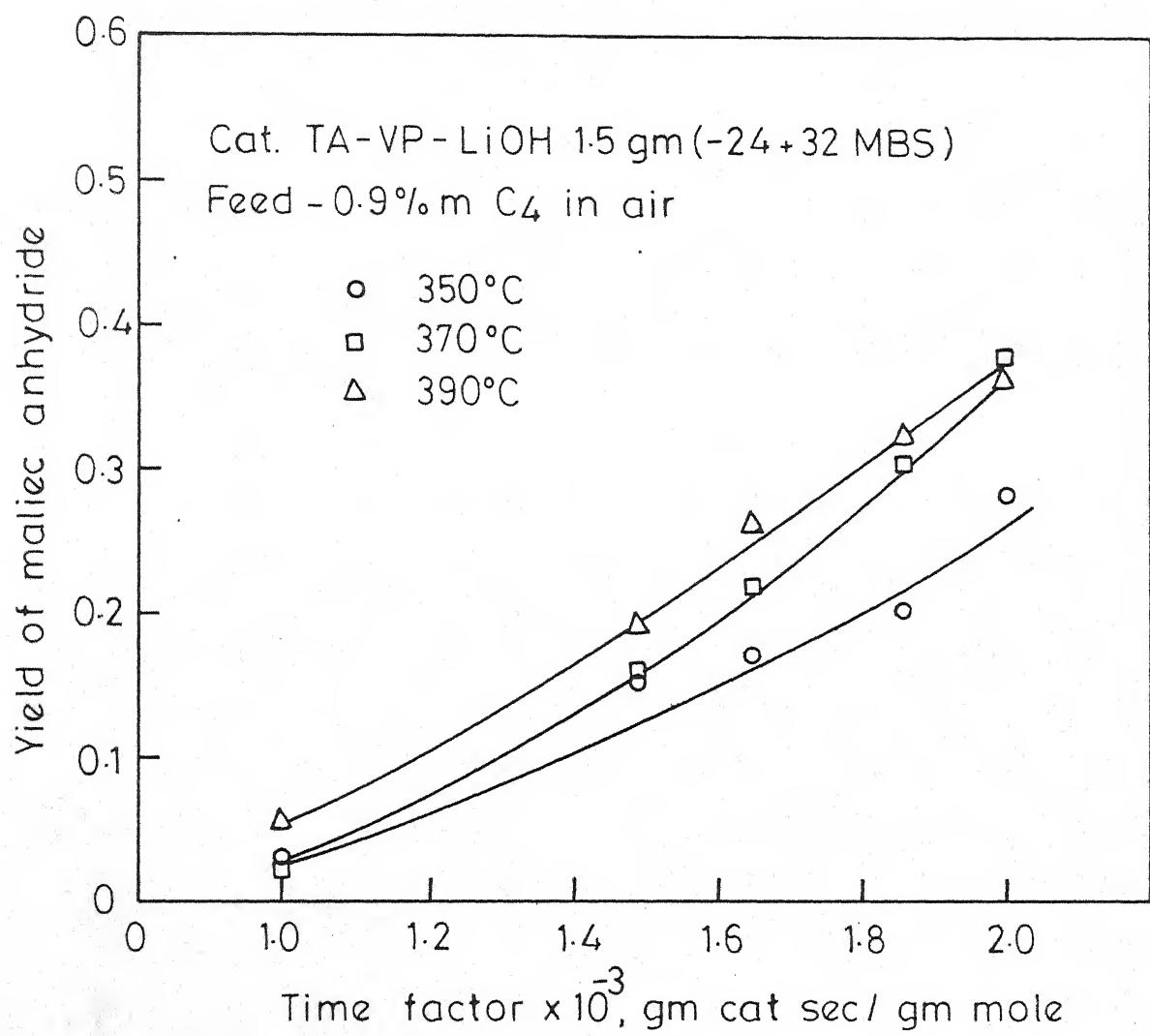
Fig. 3·7 – Yield of maleic anhydride vs. time factor.
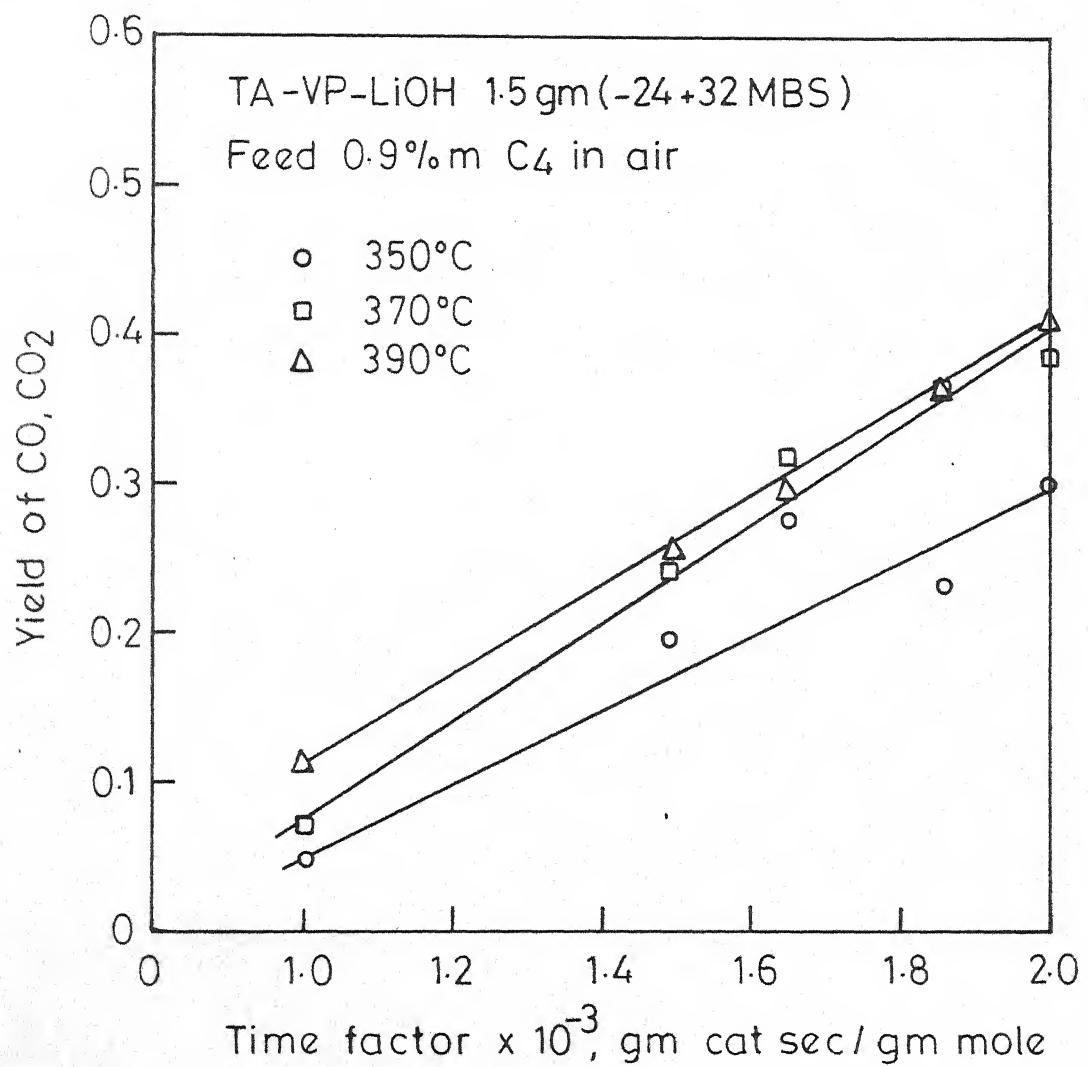
Fig. 3·8 – Yield of oxides of carbon vs. time factor.
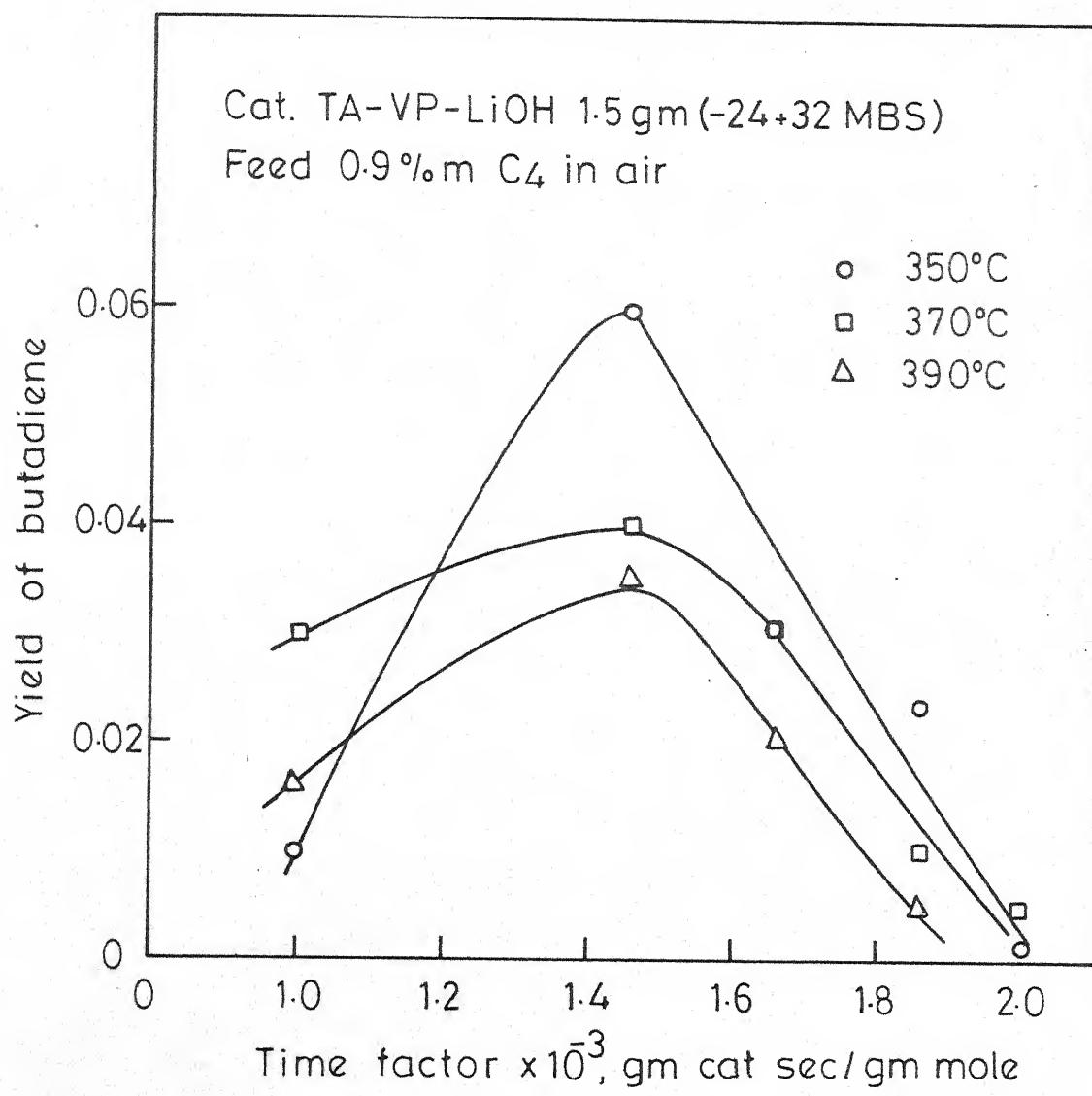
Fig.3·9 – Yield of butadiene vs. time factor.

Yield of maleic anhydride increased with increase in time factor as well as temperature Figure (3.7). Similar trend was observed in the case of oxides of carbon (Figure 3.8). Yield of butadiene was the highest at the lowest temperature studied ($350^{\circ}C$) unlike the other products (Figure 3.9).

3.2.2 Reaction Scheme:

Butene oxidation to maleic anhydride can be written down by the following reaction scheme [32].

where A_1 = $C_2H_5-CH = CH_2$

$CH_3CH = CH\ CH_3$

A_2 = $CH_2CH = CH\ CH_2$

A_3 = $C_4H_2O_3$

A_4 = $CO,\ CO_2$
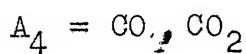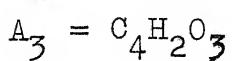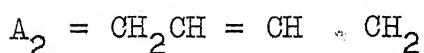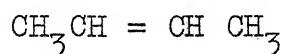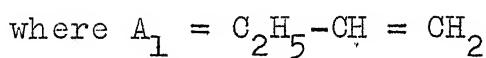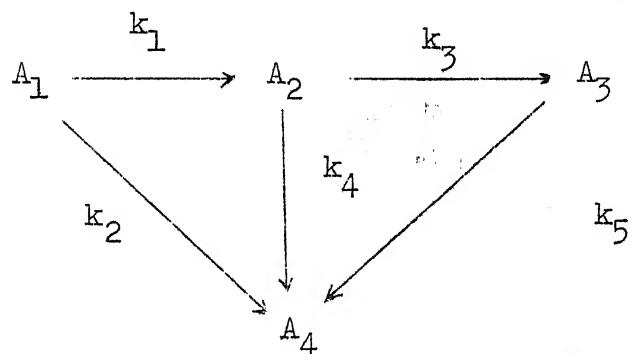
$k_1 \ldots k_5$ = rate constants.

3.2.3 Estimation of Rate Constants:

For the reaction scheme represented by the mechanism given above the pseudo first order. Kinetics may be assumed to follow and the following equations for the rate can be written:

$$R_1 = \frac{-dY_1}{d\tau_1} = (k_1 + k_2) \, p_1 \tag{3.1}$$

$$R_2 = \frac{dY_2}{d\tau_1} = k_1 p_1 - (k_3 + k_4) p_2 \tag{3.2}$$

$$R_3 = \frac{dY_3}{d\tau_1} = k_3 p_2 - k_5 p_3 \tag{3.3}$$

$$R_4 = \frac{dY_4}{d\tau_1} = k_2 p_1 + k_4 p_2 + k_5 p_3 \tag{3.4}$$

where, R_1 to R_4 = Reaction rates

$Y_1 - Y_4$ = Yield of components $A_1 - A_4$

$p_1 - p_3$ = Partial pressures of components $A_1 \ldots A_3$

Now substituting:

$$p_i = Y_i \, p_{ol} = Y_i \, N_{ol} \, P \tag{3.5}$$

$$\tau_t = \frac{W}{F_t} = \left(\frac{W}{F_{ol}} \times \frac{F_{ol}}{F_t} \right) = \tau_1 \, N_{ol} \tag{3.6}$$

where p_i = partial pressure of the component i

p_{ol} = total pressure, atmosphere

Y_i = Yield of component i

P = Total pressure atm.

W = Weight of catalyst in grams

F_t = Total molar flow rate

N_{o1} = Mole fraction of A_1 in feed

F_{o1} = Molar flow rate of component A_1 in feed g.moles/sec.

τ_t = Time factor, gm. cat. sec./gm.mole

Equation (3.1) through (3.4) can be written as

$$\frac{dY_1}{d\tau_t} = -(k_1 + k_2)\, Y_1 \tag{3.7}$$

$$\frac{dY_2}{d\tau_t} = k_1 Y_1 - (k_3 + k_4)\, Y_2 \tag{3.8}$$

$$\frac{dY_3}{d\tau_t} = k_3 Y_2 - k_5 Y_3 \tag{3.9}$$

$$\frac{dY_4}{d\tau_t} = k_2\, Y_1 + k_4 Y_2 + k_5 Y_3 \tag{3.10}$$

On integration of the above equations with the boundary conditions

$$Y_1 = 1, \quad Y_2 = 0, \quad Y_3 = 0, \quad Y_4 = 0 \text{ at } \tau_t = 0 \tag{3.11}$$

We obtain the following expressions,

$$Y_1 = e^{-k_{12}\,\tau_t} \tag{3.12}$$

$$Y_2 = \frac{k_1}{(k_{34}-k_{12})}\left[e^{-k_{12}\tau_t} - e^{-k_{34}\tau_t}\right] \tag{3.13}$$

$$Y_3 = k_1 k_3 \left[\frac{e^{-k_{12}\tau_t}}{(k_{12}-k_{34})(k_{12}-k_5)} + \frac{e^{-k_{34}\tau_t}}{(k_{34}-k_{12})(k_{34}-k_5)} \right.$$

$$\left. + \frac{e^{-k_5\tau_t}}{(k_5-k_{12})(k_5-k_{34})} \right] \tag{3.14}$$

$$Y_4 = 1 - (Y_1 + Y_2 + Y_3) \tag{3.15}$$

where $k_{12} = k_1 + k_2$

$k_{34} = k_3 + k_4$

The values of the rate constants were obtained by minimizing the objective function F defined by

$$F = \sum_{i=1}^{N} \sum_{j=1}^{M} (Y_{ij} - \hat{Y}_{ij})^2 \tag{3.15}$$

where Y_{ij} = measured value of the yield of the component i

$\hat{Y}_{ij}$ = computed value of the yield of component i

in jth experiment

N = total number of species - 1

M = total number of experiments

Box's minimization procedure was used for optimization. Computed values of the rate constants at three temperatures are given in Table 3.2.

3.2.4 Variation of rate constants with temperature:

The variation of rate constant with temperature can be best represented by Arrhenius plots (Figure 3.10). The pre-exponential factor and the energy of activation were computed for each step and are reported in the Table 3.3. Variation of rate constants follow Arrhenius behaviour since lnK vs 1/T gave astraight line.
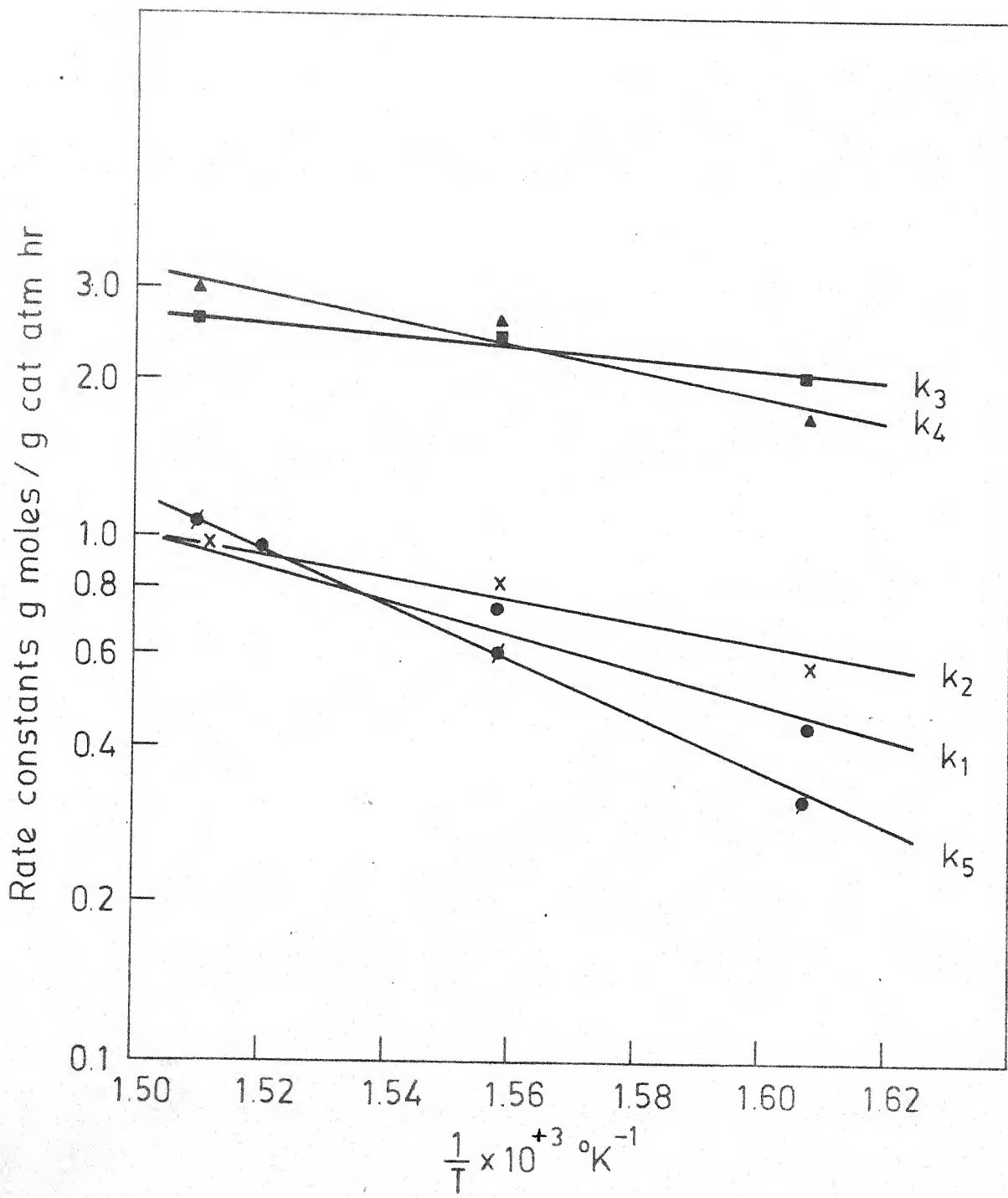
Fig. 3.10-Arrhenius plot.

TABLE 3.2

ESTIMATED VALUES OF RATE CONSTANTS

Temperature, °C	Rate constants, gmoles/g.hr.atm.					Value of F
	k_1	k_2	k_3	k_4	k_5	
350	0.43586	0.58533	2.1998	1.9982	0.3156	0.16118
370	0.72063	0.81091	2.4556	2.6003	0.6113	0.30015
390	0.95116	0.98102	2.5581	2.9999	1.0990	0.29760

TABLE 3.3

ESTIMATED KINETIC PARAMETERS

$$k_j = A_j^{\,o} \exp\left(-E_j/R_g\,T_s\right) \quad j = 1,2,3,4,5$$

Reaction Step	Energy of Activation kcal/gm. mole	Pre-exponential Factor $A_j^{\,o}$ g.moles/g. cat. atm. hr
I	11.9	0.5832×10^7
II	7.41	0.9221×10^5
III	22.9	1.2938×10^7
IV	5.75	0.3986×10^5
V	13.62	1.2261×10^6

CHAPTER 4

CONCLUSIONS AND RECOMMENDATIONS

4.1 Conclusions:

4.1.1 An essentially isothermal reactor to study the kinetics of highly exothermic reaction i.e. oxidation of butene to maleic anhydride has been constructed by using a small diameter of reactor (1/4 inch) and an efficient heat removal system a molten salt bath.

4.1.2 Effect of reducing agent in the preparation of vanadyl phosphate on the yield of maleic anhydride has been studied and d-tartaric acid has found to be superior to oxalic acid and hydrochloric acid.

4.1.3 Addition of LiOH to vanadyl phosphate catalyst increased the yield of maleic anhydride.

4.1.4 Kinetics of these reactions have been studied at the three different temperatures 350, 370 and 390°C and the rate constants and energies of activation have been calculated.

4.2 Recommendations:

Lithium hydroxide has been reported in the literature to stabilize the phosphorous in the catalyst in addition to increase the yield of maleic anhydride. Catalyst endurance

tests should be performed to verify if the catalyst having LiOH will retain its activity, and selectivity for longer time.

A microreactor should be used for kinetic analysis since this type of reactor is known to have negligible transport effects.

APPENDIX I

TABLE I.1: OXIDATION OF BUTENE UNDER THE CONDITIONS OF COMPLETE CONVERSION OF BUTENE (DATA AT 360°C)

Weight of the catalyst = 10 grams

−8+10 mesh

S.No.	Catalyst	$\tau_t \times 10^3$ $\frac{gm.cat.sec.}{gm.mole}$	Yield of maleic anhydride	Yield of carbon oxides
1	TA-VP-LiOH 360°C	2.0	0.1250	0.874
		4.1002	0.230	0.768
		8.199	0.365	0.634
		11.000	0.485	0.513
2	OA-VP-LiOH 360°C	2.0	0.095	0.903
		4.1002	0.180	0.819
		8.199	0.280	0.718
		11.00	0.370	0.627
3	TA-VP 360°C	2.0	0.10	0.889
		4.1002	0.21	0.78
		8.199	0.32	0.669
		11.00	0.42	0.568
4	HCl-VP 360°C	2.0	0.075	0.915
		4.1002	0.645	0.851
		8.199	0.205	0.793
		11.00	0.2255	0.7705

Table I.1 (contd)

OXIDATION OF BUTENE TO MALEIC ANHYDRIDE UNDER THE CONDITIONS OF COMPLETE CONVERSION (DATA AT 330°C)

S. No.	Catalyst	$\tau_t \times 10^3$ $\dfrac{gm.cat.sec}{gm.mole}$	Yield of maleic anhydride	Yield of carbon oxides
1	TA-VP-LiOH 330°C	2.0	0.0911	0.9089
		4.1002	0.175	0.8210
		8.199	0.261	0.7240
		11.00	0.325	0.6712
2	OA-VP-LiOH 330°C	2.00	0.0652	0.9309
		4.1002	0.1211	0.8774
		8.199	0.1901	0.8901
		11.00	0.2257	0.7731
3	TA-VP 330°C	2.00	0.0751	0.9231
		4.1002	0.1553	0.8443
		8.199	0.2252	0.7735
		11.00	0.275	0.7238
4	HCl-VP 330°C	2.00	0.04503	0.9486
		4.1002	0.07509	0.92371
		8.199	0.1405	0.8581
		11.00	0.1551	0.8437

TABLE I.2: ELIMINATION OF TRANSPORT EFFECTS

0.9 per cent m Butene in air at $350^{o}C$

TA-VP-LiOH   P:V:Li = 1.6:1.0:0.5 on SiO_2

S. No.	Weight of the catalyst, grams.	Size of the catalyst, B.S. Std.	$\tau_t \times 10^3$ $\frac{gm.cat.sec}{gm.mole}$	Conversion of butenes
1	2.0	−22+32	0.9416	0.2215
			1.5065	0.3755
			2.5975	0.7699
			3.7661	0.9950
2	1.5	−22+32	1.5065	0.2981
			2.0000	0.5500
			2.5000	0.7100
			3.7500	0.8600
3	2.0	−32+44	2.5031	0.7900
			1.3000	0.4616
			0.9000	0.1810
4	1.5	−32+44	1.2551	0.2826
			2.2650	0.6310
			3.1254	0.8255

TABLE I.4

SELECTIVE OXIDATION OF BUTENES TO MALEIC ANHYDRIDE DATA
OBTAINED UNDER CONDITIONS OF INCOMPLETE CONVERSION
OF BUTENES

Catalyst — TA-VPLiOH   P:V:Li = 1.6:1.0:0.5,   0.9 per cent m
butene in air

Temperature, °C	$\tau_t \times 10^3$ gm.cat.sec / gm.mole	Butenes	Butadiene	Maleic anhydride	Oxides of carbon
			Yield of		
	1.00	0.910	0.010	0.03	0.048
	1.49	0.585	0.060	0.15	0.199
350	1.66	0.510	0.035	0.17	0.275
	1.86	0.540	0.025	0.20	0.233
	2.00	0.420	0.001	0.28	0.297
	1.00	0.890	0.030	0.02	0.070
	1.49	0.560	0.040	0.16	0.241
370	1.66	0.440	0.030	0.22	0.317
	1.86	0.320	0.01	0.305	0.365
	2.00	0.230	0.005	0.380	0.386
	1.00	0.800	0.016	0.055	0.110
	1.49	0.510	0.035	0.190	0.250
390	1.66	0.420	0.020	0.260	0.290
	1.86	0.295	0.005	0.320	0.360
	2.00	0.2216	–	0.360	0.410

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